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Spectrophotometric Study of Complexation Between Some New N₂O₂-Schiff Bases and Some Transition Metal Ions in Nonaqueous Solvents

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Abstract: The complexation reaction between some transition and heavy metal cations and some new N_2O_2 Schiff bases in acetonitrile (AN) or methanol (MeOH) as nonaqueous solvents at 25 °C and 0.05 M tetraethylammonium perchlorate (TEAP) were investigated by spectrophotometric method. The stoichiometry and overall stability constants of complexes have been evaluated by computer refinement of abs-mole ratio data, using the KINFIT program. All investigated metal ions form 1:1 ML, 1:2 ML₂ or 2:1 M₂L complexes with studied ligands. The effect of structure on the complexation was investigated.

Keywords: Complexation, N₂O₂-Schiff bases, Acetonitril, Transition metal ion.

Introduction

During the past two decades, considerable attention has been paid to the chemistry of the metal complexes of Schiff bases containing nitrogen, oxygen and sulfur donor atoms¹⁻³. This may be attributed to their stability, biological activity and potential applications in many fields such as oxidation catalysis and electrochemistry. Azomethine compounds have wide applications in many biological aspects, *viz.*, proteins⁴, visual pigment⁵. Schiff base transition metal complexes are one of the most versatile and thoroughly studied systems^{6,7}. Particularly, complexes of divalent transition metal ions involving derivatives of salicylaldehyde and aliphatic amines are important, because of their similarity to the biological dioxygen carriers^{8,9}, their applications in the clinical¹⁰, analytical fields^{11,12} and non-enzymatically controlled transamination reactions¹³.

The study of complexation reaction of these ligands in non-aqueous matrices could be used as an efficient strategy to design the analytical systems such as potentiometric sensor¹⁴⁻¹⁶, bulk and supported liquid membrane transport^{17,18}, optical sensor¹⁹, solid phase and cloud

point extraction^{20,21} and biochemistry fields²². Thus, the studies of complexation reaction of these Schiff bases with metal ions, not only result effective information about complexation, but also lead to a better understanding of the selectivity of these ligands toward different metal cations.

It is important for an analytical chemist to know what kind of complexes with what stability may be expected. Knowledge of the composition of a solution in terms of the species formed is of importance in many parts of solution chemistry: in understanding analytical procedures, industrial process, pollution of natural waters and biological fluids. Knowledge of the equilibria is also of importance for interpretation of the kinetics of reactions in solution.

The aim of comparative studies of the various equilibrium processes in virtually all cases is to find a correlation between the values of the equilibrium constants and the parameters reflecting the chemical properties of the components participating in the process. Basically two types of the parameters reflecting the chemical properties are distinguished: (a) physical parameters due to the interaction of the component in question with physical fields (*e.g.* ionization potential, electroaffinity, ionic potential, polarizability) and (b) correlation coefficients expressing the connection between the various chemical properties, which can be determined from a large number of studies (*e.g.* Hammet σ value, electronegativity, data reflecting the hard-soft nature, *etc.*)²³.

We have used the Kinfit and Best program^{20,24-27}, for evaluating the stability constant of complexes using the spectrophotometric and potentiometric data respectively²⁸⁻³². Of particular interest have been those involving Schiff base since they reveal surprising molecular diversity not only in coordination geometry but in more subtle changes in the ligands.

In the present work the authors decided to investigate spectrophotometric study and the effect of the ligands structure on the stability constants of the complexation of the some metal ions with various salophen and salpn derivatives. Based on this data, one can focus to synthesize new ligands with proper stability constant toward metallic ions for the selective and sensitive determination of metal ions.

Experimental

Analytical grade nitrate salts of Cu(II), Ni(II), Co(II), Zn(II), UO₂(II), La(III), Ce(III) and Th(IV) ions are purchased from Merck Company and used without any further purification. Tetraethylammonium perchlorate (TEAP) was synthesized according to literature³³. The ligands, including bis(hydrosalicylate) 1,3-propanediimine (BSAPD), bis(salicylaldehyde) 1,2-phenylenediimine (BSPHEN), bis(salicylaldehyde) 4-nitro1, 2-phenylenediimine (BSNPHEN), bis(salicylaldehyde)4-carboxylic-1,2-phenylendiimine (BSCPHEN) was synthesized according to literature³⁴⁻³⁶ and the ligands bis(2-hydroxyphenyl) 1,2-phthaldimine (BHPPDI), bis(2-hydroxyacetophenone) ethylenediimine (BHAED), bis(2-hydroxyacetophenone)-1,4-butanediimine (BHABDI) prepared according to procedure given below.

Preparation of bis(2-hydroxyphenyl)1,2-phthaldiimine (BHPPDI)

5 mmol of 2-Aminophenol and 2.5 mmol of phthaldialdehyde in 25 mL ethanol was gradually added to a 25 mL ethanolic solution and the reaction mixture was refluxed. The progress of the reaction was monitored by TLC (Thin layer chromatography). After 8 h, 50 mL cooled water was added to reaction mixture. Deep yellow precipitate was filtered and washed with water and ethanol/water mixture. Thus bis(2-hydroxyphenyl) 1, 2-phthaldiimine

(BHPPDI) was obtained in 76% yield. M.p is 117-120 °C. Elemental analysis: calculated (%) $C_{20}H_{16}N_2O_2$: C 48.93; H 4.62; N 7.13. Found: C 49.27; H 4.72; N 6.96. Characteristic IR(KBr, cm⁻¹): 3306 (bs, vOH), 3061 (w, CH- Aromatic), 2976(w, CH-imine), 1634(vs, vC=N- imine) 1493(s),1586(s), 1453(s, vC=C, aromatic ring), 1331(m), 1302(m), 1274(m), 1209 (m, vC-N), 1146(m), 1123(w), 1033(m, C-O), 928(w), 896(m), 747(s), 727(s), 657(m), 566(w), 471(m). UV (CH₂Cl₂, λ_{max}): 223 and 306 nm. ¹H NMR (DMSO-d₆, ppm): 10.22(bs, 1H), 8.88 (bs, 1H), 7.57 (m, 4H), 7.16 (m, 2H), 6.93(m, 2H), 6.61(m, 2H) and 6.35(m, 4H) ppm.

Preparation of bis(2-hydroxyacetophenone)ethylenediimine (BHAED)

To 1 mmol (0.12 g) of eyhylenediamine in 50 mL ethanol, 2 mmol (0.544 g) of 2-hydroxy acetophenone was added in 50 mL ethanol. The reaction mixture was refluxed for 7 h. Then the mixture was kept in refrigerator overnight and then filtered to give the product as yellow crystals (86% yield). The product was characterized by physical and spectral data.

IR (KBr, cm⁻¹) : 3444(bs, vOH), 3053(w, CH- Aromatic), 2935(w, CH- aliphatic), 2837 (w, CH- aliphatic), 1609 (-C=N), 1575 (C=C), 1507 (m, C=C), 1445, 1366 (s), 1325 (m), 1312 (s), 1292 (s), 1261 (m, vC-N), 1240 (m), 1198 (m), 1160 (s), 1128 (m), 1064 (s,C-O), 1024 (s,C-O), 947 (m), 859 (m), 836 (m), 757 (s), 743 (m), 648 (m), 557 (m), 524 (m), 503 (m), 467 (m), 451 (m), 440 (m), 407 (m). ¹H NMR (CDCl₃): 15.64 (s, 2H), 7.32 (t, 2H, J= 7.95Hz, J= 6.95Hz), 7.04 (m, 2H), 6.62 (d, 2H, J= 8.30Hz), 6.57 (t, 2H, J= 7.20Hz, J= 7.90Hz), 3.75 (s, 4H), 2.16 (s, 6H) ppm. ¹³C NMR (CDCl₃/DMSO): 173.01, 163.36, 132.62, 128.51, 119.68, 118.52, 117.59, 77.91(t, CDCl₃), 50.34, 40.37 (q, DMSO-d₆), 15.07 ppm. UV-Vis (CHCl₃): 308, 370 nm. M.p 58 °C.

Preparation of bis(2-hydroxyacetophenone)-1,4-butanediimine (BHABDI)

2 mmol of 2-Hydroxy acetophenone was added to 1.0 mmol of 1,4-butanediamine and the reaction mixture was refluxed for 6 h. Then the mixture was kept in refrigerator overnight and filtered to obtain yellow crystals of product (89% yields). The product was characterized by different analytical techniques. Elemental analysis, $C_{20}H_{24}N_2O_2$: (theoretical values of C 74.04%; H 7.46%; N 8.64%), while found: C 74.21%; H 7.38% and N 8.69%. Infra red spectra (KBr, cm⁻¹): 3433(br s, m OH),3048 (w, CH–aromatic), 2933 (w, CH–aliphatic), 2866 (w, CH–aliphatic),1613 (–C=N), 1554 (C=C), 1492 (m, C=C), 1444 (m),1382 (w), 1325 (m), 1311 (m), 1231 (m), 1261 (m, mC–N), 1159 (s),1130 (m), 1068 (m, C–O), 1009 (m, C–O), 948 (m), 841(s), 836 (m),761 (s), 746 (s), 633 (m), 560 (m), 526 (m), 474 (m) and 443 (w).

Spectrophotometric titration

Standard stock solutions of ligand $(1.0 \times 10^{-3} \text{ M})$ and the metal ions $(1.0 \times 10^{-3} \text{ M})$ were prepared by dissolving appropriate and exactly weighed (with an accuracy of ±0.0001 g) amount of pure solid compounds in pre-calibrated 25.0 mL volumetric flasks and diluted to the mark with solvent. Working solutions were prepared by appropriate dilution of the stock solutions. According to the spectra reported (Figures 1-5), titration of the ligand solution (for sample 3.8×10^{-5} M, 2.6 mL) was carried out by the addition of micro-liter amounts of a concentrated standard solution of the metal ion $(1.0-2.5 \times 10^{-3} \text{ M})$ using a pre-calibrated micro-syringe, followed by absorbance intensity reading at 25.0 °C and 0.05 M TEAP.

Results and Discussion

Complexation of transition and heavy metal cations with donor atoms such as nitrogen and sulfur or hard atoms such as oxygen is favored, These ligands, play a key role in the speciation of metal ions in various media and in controlling its physicochemical behavior,

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biological availability, accumulation and mobility. Depending on the pH value, presence of salts (ionic strength effect) and degree of saturation of binding sites, ligands substances can form either soluble or insoluble complexes with various metal ions and play a double role in various matrixes The stability of a transition metal complex with a polydentate chelate ligand depends on a range of factors including: number and type of the donor atoms present and the number and size of the chelate rings formed on complexation³⁷. In addition, the stability and selectivity of complexation strongly depend on the donor ability and dielectric constant of the solvent³⁸ and shape and size of the solvent molecules³⁹.

In detail the complexation of some transition metal ions with some ligands including BHAEDI, BSAPD, BHABDI, BSPHEN, BSNPHEN, BSCPHEN, BHPPDI (Table 1) and their stability constant and stoichiometry has been calculated using KINFIT program.



Table 1. Structure of ligands

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Investigation of complexation

Nonaqueous solvents usually are more inert toward ions than water. It would seem that the more intrinsic properties of solutes could be more readily established in non-aqueous media, since many of the unusual properties of water as a solvent are absent in the former media. Nonaqueous studies would be useful also in understanding the nature of solutes that have only a limited solubility in water. In addition the pH of solution must be controlled in water solution for reasons such as the above; studies of nonaqueous solutions systems have been undertaken.

The interaction of some Schiff bases with the metal ions was studied by adding various ratio of metal ions solution in acetonitrile or methanol. The structure of studied Schiff base ligands and abbreviation of their names and spectra characteristic are summarized in Table 1. The complexation of these ligands was carried out spectrophotometrically in methanol and acetonitrile medium by mole ratio method. In these experiments, ligand concentration was kept constant and metal ion concentration was increased of M/L ratio from 0-4 in excess. The respective curves are presented in Figures 1-5. The increase in the concentration of the transition metal ions causes that one of the original peaks of the Schiff base ligand at about 250-285 nm gradually vanished and the other original peak around 300-380 nm shifted to lower wavelengths with the increase in its intensity and a new peak appeared at about 400-500 nm its intensity increases with the increase in the concentration of metal ions with very clear isosbestic points. As it was reported in Table 1, one of the bands in 300-370 nm range in the spectrum of the ligand was assigned to $\pi \rightarrow \pi^*$ transition of the imine nitrogen atom in conjugation with the phenoxy group⁴⁰. The other absorption bands associated with the $\pi \rightarrow \pi^*$ transition of the phenoxy group shifted by about 10 nm the bathochromic shifting of ligand peaks indicate coordination of metal ion with the ligand chromophoric groups.



Figure 1. UV-Vis spectra for titration of BHAED (a) and BSPHEN (a') $(3.8 \times 10^{-5} \text{ M})$ with UO₂²⁺ ion in acetonitrile (T = 25 °C, I= 0.05 M and 0.05 M TEAP) and the corresponding absorbtion mole ratio curves at 362, 420 nm respectively (b,b') and curve fitting (c,c').





Figure 2. UV-Vis spectra for titration of BHABD (a) and BSAPD (a') $(3.8 \times 10^{-5} \text{M})$ with Co²⁺ ion in acetonitrile (T = 25 °C, I= 0.05 M and 0.05M TEAP) and the corresponding absorbtion mole ratio curves at 372, 272 nm respectively (b,b') and curve fitting(c,c')



Figure 3. Uv-Vis spectra for titration of BSNPHEN $(3.8 \times 10^{-5} \text{ M})$ with metal ions $(1.0 \times 10^{-3} \text{ M})$ (a) Cu²⁺, (b) Ni²⁺, (c) Co²⁺ and (d) UO₂²⁺ ion in acetonitrile (T=25 °C and I= 0.05 M TEAP)



Figure 4. UV-Vis spectra for titration of BSCPHEN $(3.8 \times 10^{-5} \text{ M})$ with metal ions containing (1.0×10^{-3}) (a) Cu²⁺, (b) Ni²⁺, (c) Co²⁺ and (d) UO₂²⁺ in acetonitrile (T=25 °C and I= 0.05 M TEAP)



Figure 5. UV-Vis spectra for titration of BHPPDI $(3.8 \times 10^{-5} \text{ M})$ with metal ions containing (1.0×10^{-3}) (a) Cu²⁺, (b) Ni²⁺ (c) and Co²⁺ ion in acetonitrile (25 °C and I = 0.05 M TEAP)

The appearance of band at higher wavelength with higher intensity may be attributed to coordination of imine nitrogen atoms to the metal ion with an additive effect due to deprotonated phenolate groups upon chelation. The absorption at about 400-550 nm is assigned to a ligand-metal d- π^* charge transfer transition⁴¹⁻⁴³. Additional band at 254 nm is inter-ligand $(\pi - \pi^*)$ transition centered on coordinated Sciff base. The band at about 280 nm was assigned to a phenyl ring $\pi - \pi^*$ transition ^{44,45}. The shifting of ligand peaks towards lower energy on deprotonation of the chelating units can be explained by two ways: (i) the interaction of enolimine with a hydrogen-bond forming solvent would presumably reduce the O- H bond strength and facilitate proton transfer to the nitrogen center favouring the formation of the ketoamine, which gives characteristic $n \rightarrow \pi^*$ transition at longer wavelength than the corresponding enolimine; (ii) on deprotonation, formation of phenolate ion from phenol stabilized the $\pi \rightarrow \pi^*$ excited state due to charge delocalization and brings the lowest excited state closer to the highest ground state and thus permits a lower energy (longer wavelength) for transition. Analyses of spectra using KINFIT whole at maximum wavelengths gave the best fit of absorbance moleratio data (for sample Figure 1-c,c' and 2c,c) for ML and ML₂ complex and its formation constants with their standard deviations are given in Tables 2 and 3 for sample of plot fitting are brought The possibility of other type of formulations in Figures 1, 2- c, c' were ruled out due to absence of any extra peak in the higher wavelengths, which was further confirmed as inclusion of additional species in the model The complexation through two tertiary imine groups followed by two phenolate groups to give a uncharged four-coordinated ML species with distorted octahedral structure, where two-coordination sites are occupied solvent water molecules at *cis*-position in solid state. It has been shown for a (N, O-donor) tetradentate Schiff base ligand, the relative flexibility of these ligands allow formation of metal complexes to give a 'umbrella' or 'stepped' like geometry the stoicheimetry of complex for metal ions are ML or ML and ML_2 . The authors think that the uranyl ion formation of M_2L complex with BSCPHEN is due to the probability of inserting one uranyl ion to the ligand cavity and the another interact

with carboxilate to form ML. About the ligand BHPPDI, the stoichiometry for copper(II), nickel(II) and cobalt(II) is ML and ML_2 . This fact may be due to steric distortion of ligand so that the ligand acts as a bidentate that lead to formation of ML_2 in agreement to previously reports⁴⁶⁻⁴⁹

Ligand	solvent	Metal ion	$\log \beta_1$	$\log \beta_2$	M/L
BHAED	AN	Cu ²⁺	6.02±0.01	9.33±0.01	1:1&1:2
		Ni ²⁺	4.03±0.01	8.04±0.01	1:1&1:2
		Co ²⁺	4.99 ± 0.02		1:1
		Mn ²⁺	5.00±0.01	9.00±0.01	1:1&1:2
		Cd^{2+}	4.06±0.01	7.93±0.01	1:1&1:2
		UO_{2}^{2+}	5.78 ± 0.01	9.80±0.01	1:1&1:2
		Th ⁴⁺	4.00±0.02	7.01±0.05	1:1&1:2
	MeOH	La ³⁺	5.23±0.02		1:1
		Fe ³⁺	6.11±0.20		1:1
BHABDI		Cu ²⁺	5.00±0.24		1:1&1:2
	AN	Ni ²⁺	0.2625.01	9.01±0.47	1:1&1:2
		Co ²⁺	4.89±0.23		1:1&1:2
	MeOH	Zn^{2+}	5.92 ± 0.29		1:1&1:2
		Fe ³⁺	4.99±0.26		1:1&1:2
		Cr ³⁺	5.01±0.42	9.01±0.56	1:1&1:2
BSAPD	AN	Co ²⁺	5.00 ± 0.01	4.00 ± 5.01	1:1&1:2
		Zn^{2+}	5.76±0.01	10.51±0.0	1:1&1:2
		Cu ²⁺	5.56±0.01	8.72±0.01	1:1&1:2
		Ni ²⁺	6.06±0.43		1:1
		Pb ²⁺	3.95±0.01	6.96±0.01	1:1&1:2
	MeOH	Cr ³⁺	4.59±0.12		1:1

Table 2. The overall stability constants of complexation between some metal ions with BHAED, BHABDI and BSAPD at 25 °C and 0.05 M TEAP in acetonitrile or methanol solvent

The Schiff base ligands BSCPHEN and BSHNPDI and substituted BSPHEN were chosen according to their structures by changing both the aldehyde and the amine parts and changing the substitution in order to study their influence on the metal coordination sphere. The differences among the stability constants values are probably due to the change in the nature of the metal environment in the four complexes and the interior core of desired complexes. In our view, the higher core of BSPHEN and flexibility suitable and superior it for complexation with metal ions in comparison to BHPPDI. In fact, the presence of the primary amine nitrogen in the metal coordination sphere may lead to ligand distortion in the both complexes, unlike the less rigid BHNPDI complexes reduce the stability constant. The result of stability constant of Schiff base with metal ion show that salophen has higher stability in comparison to other derivatives such as BSNPHEN and BSCPHEN, that may be atributed to the fact that withdrawing group such as carboxilic and nitro in the ligand reduce their activity for complexation. The order for stability constant of the mentioned ligands for every metal ion is as following BSCPHEN<BSNPHEN<As it can be seen from Table 3, the complex between BSCPHEN and metal ion has lower stability constant with respect to other ligands. In a view glance to the result of stability constant one can notice that the stability constant for BSNPHEN is higher than respective value for BSCPHEN. This can be explained that in the presence of nitro with higher electron withdrawing property the intra- molecular hydrogen bond will be weakened. In the salophen ligand, a strong intramolecular hydrogen bond between iminic nitrogen and phenolic hydrogen exist that will be distroyed by complexation. Nitro group with higher electron withdrawing tendency decrease the strength of intra-molecular hydrogen bond, therefore facilitate the complex formation and lead to higher stability constant due to decrease in activity of BSCPHEN ligand.

In Schiff base ligands of BSPHEN and BHPPDI the more resonance and interior core of ligands favor their complexation with metal ion, while more rigidity and higher interior core of ligands in BSPHEN increased the complexation probability and its stability constant.

Table 3. The overall stability constants of complexation between some metal ions with BSPHEN, BSNPHEN, BSCPHEN and BHPPDI at 25 $^{\circ}$ C and 0.05 M TEAP in acetonitrile

Ligand	Metal ion	$\log \beta_1$	$\log \beta_2$	M/L
BSPHEN	Cu ²⁺	8.30±0.30		1:1
	Ni ²⁺		9.91±0.40	2:1
	Co ²⁺	7.40±0.14		1:1
	UO_{2}^{2+}	5.80±0.11		1:1
DENDLIEN	Cu ²⁺	8.01 ± 0.23		1:1
	Ni ²⁺		8.92 ± 0.15	2:1
DOINFHEIN	Co ²⁺	6.80 ± 0.20		1:1
	UO_{2}^{2+}	4.72 ± 0.20		1:1
	Cu ²⁺	7.01 ± 0.12		1:1
DSCDUEN	Ni ²⁺	5.81 ± 0.10		1:1
DSCILEN	Co ²⁺		10.20 ± 0.21	1:2
	$\mathrm{UO_2}^{2+}$		9.88 ± 0.15	2:1
BHPPDI	Cu ²⁺	6.00 ± 0.10	9.00 \pm 0.10	1:1 & 1:2
	Ni ²⁺	5.15 ± 0.12	8.15 ± 0.14	1:1 & 1:2
	Co ²⁺	4.90 ± 0.08	7.90 ± 0.11	1:1 & 1:2

As it is seen from Table 2, the results of complexation between the L_1 (BHAED), L_2 (BHABDI) and L_3 (BSAPD) ligands and metal ion revealed the order of stability $L_2>L_1>L_3$ almostly. The low stability complexes of L_3 relative to L_2 and L_1 refer to the presence of two methyl group, in the structure of L_1 and L_2 . In comparing complexes of L_1 and L_2 with metal ions, the stability constants of L_2 is relatively high to L_1 , due to the presence of longer hydrocarbon chain, which causes to distort of flexibility in structure. The order for stability of metal ion-Schiff base complexes, are agreement with the Irving Williams⁵⁰ order, but this ranking in some cases was not observed.

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